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The continuous wave electron paramagnetic resonance experiment revisited

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Abstract

When the modulation frequency used in continuous wave electron paramagnetic resonance (cw EPR) spectroscopy exceeds the linewidth, modulation sidebands appear in the spectrum. It is shown theoretically and experimentally that these sidebands are actually multiple photon transitions, $\sigma^+ + k \times \pi$, where one microwave (mw) σ^+ photon is absorbed from the mw radiation field and an arbitrary number k of radio frequency (rf) π photons are absorbed from or emitted to the modulation rf field. Furthermore, it is demonstrated that both the derivative shape of the lines in standard cw EPR spectra and the distortions due to overmodulation are caused by the unresolved sideband pattern of these lines. The single-photon transition does not even give a contribution to the first-harmonic cw EPR signal. Multiple photon transitions are described semiclassically in a toggling frame and their existence is proven using second quantization. With the toggling frame approach and perturbation theory an effective Hamiltonian for an arbitrary sideband transition is derived. Based on the effective Hamiltonians an expression for the steady-state density operator in the singly rotating frame is derived, completely describing all sidebands in all modulation frequency harmonics of the cw EPR signal. The relative intensities of the sidebands are found to depend in a very sensitive way on the actual rf amplitude and the saturation of single sidebands is shown to depend strongly on the effective field amplitude of the multiple photon transitions. By comparison with the analogous solutions for frequency-modulation EPR it is shown that the field-modulation and the frequency-modulation technique are not equivalent. The experimental data fully verify the theoretical predictions with respect to intensities and lineshapes.

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1. Introduction

Since the beginning of magnetic resonance spectroscopy modulation of the static magnetic field and phase-sensitive detection have been used to reduce the noise in measurements of weak continuous wave (cw) signals [1]. While in nuclear magnetic resonance (NMR) the cw technique has been replaced by pulsed techniques, it is still the most frequently used experimental method in electron paramagnetic resonance (EPR).

Due to modulation, cw EPR spectra can deviate from the derivative of the absorption spectrum predicted by the commonly used simple modulation theory. Distortions arise when the modulation amplitude or the modulation frequency are larger than the linewidth. In the latter case sidebands appear in the spectrum, which were explained classically by using modified Bloch equations [2]. Although the results describe the observed effects correctly, they give no insights into the physical process behind this phenomenon.

A first attempt to explain modulation-induced sidebands quantum mechanically was made by Miyagawa et al. [3]. Modulation-induced sidebands are also closely

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